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Large Micro-Sized $\text{K}_2\text{TiF}_6$:$\text{Mn}^{4+}$ Red Phosphors Synthesised by a Simple Reduction Reaction for High Colour-Rendering White Light-Emitting Diodes

Tao Han$^a$, Tianchun Lang$^a$, Jun Wang$^a$, Mingjing Tu$^a$ and Lingling Peng$^a$

A simple chemical method for synthesising large micro-sized $\text{K}_2\text{TiF}_6$:$\text{Mn}^{4+}$ phosphors (50-100 μm) is presented, based on a direct reduction reaction with $\text{K}_2\text{TiF}_6$ particles immersed in $\text{KMnO}_4$-$\text{HF}$ solution. The Mn$^{4+}$ concentration in $\text{K}_2\text{TiF}_6$ primarily increases as the initial $\text{KMnO}_4$ concentration is increased, subject to the diffusion of Mn$^{4+}$ ions. However, the relative emission intensity of our synthesised $\text{K}_2\text{TiF}_6$:$\text{Mn}^{4+}$ is first enhanced and then declines with increasing $\text{KMnO}_4$ concentration, with an optimum $\text{KMnO}_4$ concentration of 0.016 g/ml, which most likely depends on the concentration quenching effect.

The synthesised $\text{K}_2\text{TiF}_6$:$\text{Mn}^{4+}$ (0.35-4.4 at.%) phosphors show good thermal stability and can be adopted to fabricate high CRI (Ra > 85) white LEDs for indoor lighting.

1. Introduction

Solid state lighting based on light-emitting diodes (LEDs) will replace all incandescent bulbs and compact fluorescent lamps, due to their energy-saving, environmentally friendly, and long-lasting features.\(^1\)\(^2\)

Until now, an InGaN chip (emitting near 460 nm) combined with a yellow phosphor. The solution can produce warm-white light (CCT=2840 K) and a sufficiently high CRI (Ra=80-96).\(^3\)\(^4\)

Here, we report a simple reduction reaction for synthesising large micro-sized $\text{K}_2\text{TiF}_6$:$\text{Mn}^{4+}$ red phosphors. We demonstrate that the Mn$^{4+}$ concentrations in the $\text{K}_2\text{TiF}_6$ host are 3.7-5.3 at.% (approximately 50 at.% Mn$^{4+}$ reduced to Mn$^{2+}$) and that the emission spectrum of the obtained $\text{K}_2\text{TiF}_6$:$\text{Mn}^{4+}$ consists of five narrow bands, extending from 580 to 660 nm, with the strongest peak at 634.8 nm (~2 eV). Upon the addition of the synthesised $\text{K}_2\text{TiF}_6$:$\text{Mn}^{4+}$, the fabricated white LED exhibits a high CRI (Ra > 85) and is thus suitable for indoor lighting.

2. Experimental

$\text{K}_2\text{TiF}_6$ (AR), $\text{KMnO}_4$ (AR), $\text{KF}$-$\text{H}_2\text{O}$ (AR), HF solution (≥40 wt.%) and $\text{H}_2\text{O}_2$ solution (≥30 wt.%) were purchased from the Tianjin Yongda Chemical Reagent Company, Limited, China. All of the chemicals were used directly without further purification.

$\text{K}_2\text{TiF}_6$:$\text{Mn}^{4+}$ phosphors were synthesised by a simple reduction reaction. Typically, a certain amount of $\text{KMnO}_4$ powder and $\text{KF}$-$\text{H}_2\text{O}_2$ crystals were combined in 5 ml of HF solution, and then, 3.0 g of $\text{K}_2\text{TiF}_6$ particles was added to form a purple mixture. Next, 10 wt.% $\text{H}_2\text{O}_2$ solution was slowly dropped into the obtained purple mixture under stirring. Finally, the products were separated by vacuum filtration and rinsed in 10 wt.% HF solution and ethanol.

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The crystalline structures of the samples were analysed using an X-ray diffractometer (XRD-6000, Shimadzu) with Cu Ka1 radiation (λ=0.154187 nm). Powder XRD data were collected in scanning mode for a 2θ range of 10° to 80° with a step of 0.02° and a rate of 2.0° min<sup>-1</sup>. Unit cell refinements were accomplished using JADE software. The morphologies of the samples were acquired using a scanning electron microscope (Quanta 250, FEI) with an accelerating voltage of 10 kV. X-ray photoelectron spectra (XPS) were collected using an electron spectrometer (V4105, Thermo Electron).

The chemical element analyses present in the materials at the microscopic level were performed by energy dispersive X-ray spectrometry (ICP–OES) (OPTIMA 2000DV, Perkin Elmer). The crystalline structures of the samples were analysed using an X-ray diffractometer (XRD-6000, Shimadzu) with Cu Kα1 radiation in scanning mode for a 2θ range of 10° to 80° with a step of 0.02° and a rate of 2.0° min<sup>-1</sup>. Unit cell refinements were accomplished using JADE software. The morphologies of the samples were acquired using a scanning electron microscope (Quanta 250, FEI) with an accelerating voltage of 10 kV. X-ray photoelectron spectra (XPS) were collected using an electron spectrometer (V4105, Thermo Electron).

The absorption spectrum of BaSO<sub>4</sub> measured by the F-7000 fluorescence spectrophotometer equipped xenon lamp as the excitation source. The quantum efficiencies were performed using an inductively coupled plasma optical emission spectrometry (ICP–OES) (OPTIMA 2000DV, Perkin Elmer). The photoluminescence properties of the samples were measured by a fluorescence spectrophotometer (F-7000, Hitachi) with a 150-W xenon lamp as the excitation source. The quantum efficiencies were measured by the F-7000 fluorescence spectrophotometer equipped with an integrating sphere at the room temperature. In the determination, the samples were placed in a metal cell, and then absorption spectrum of BaSO<sub>4</sub> white reflectance standard sample, absorption spectrum of samples, and emission spectrum of samples were obtained, respectively. The internal (external) quantum efficiency was calculated by QuantumYields tool with the ratio of the number of photons in the emission spectrum to that in the absorption (excitation) spectrum. The temperature quenching property was detected by thermocouples inside the plaque and was controlled with a standard high-temperature fluorescence controller (TAP-02, Orient KOJI). The luminous efficiency, colour-rendering index, and the Commission Internationale de l’Eclairage (CIE) colour coordinates of the fabricated LEDs were characterised using a high-accuracy LED photo-colour and electron test system (HSP3000, Hangzhou Hongpu Optoelectronics Technology Co. Ltd., China) and were evaluated under a current of 90 mA.

3. Results and discussion

According to the literature, the cation exchange reaction is a convenient method for preparing Mn<sup>4+</sup>-activated fluoride phosphors. However, the main difficulty in synthesising Mn<sup>4+</sup>-activated fluoride compounds lies in the diverse valence states of Mn, including Mn<sup>2+</sup>, Mn<sup>3+</sup>, and Mn<sup>4+</sup>. Of these, Mn<sup>4+</sup>-activated fluoride phosphors measured by excitation at 325 nm reveal a single broad emission peak at ~585 nm (T<sub>1</sub>→A<sub>1</sub>), and Mn<sup>4+</sup>-doped crystals exhibit optical absorption in the spectral region from the near IR to UV, with near-IR luminescence observed at ~1100 – 1300 nm at very low intensities. In addition, the Mn<sup>4+</sup> ion is not an efficient activator in most host insulators.

K<sub>2</sub>FeF<sub>6</sub> can be synthesised by a simple chemical reaction as follows:

\[
2\text{KMnO}_4 + 2\text{KF} + 10\text{HF} + 3\text{H}_2\text{O} \rightarrow 2\text{K}_2\text{MnF}_6 + 8\text{H}_2\text{O} + 3\text{O}_2. \tag{1}
\]

However, the synthesised fluoride compound is K<sub>2</sub>MnF<sub>6</sub>:H<sub>2</sub>O in aqueous solution. Thus, Equation (1) is one of the intermediate reactions in the process for reducing KMnO<sub>4</sub> in HF solution by H<sub>2</sub>O<sub>2</sub>. Based on this fact, we developed a simple method for synthesising K<sub>2</sub>TiF<sub>6</sub>:Mn<sup>4+</sup>. The synthesis was performed by mixing KMnO<sub>4</sub>, KF-2H<sub>2</sub>O and K<sub>2</sub>TiF<sub>6</sub> in HF solution, with H<sub>2</sub>O<sub>2</sub> as a reducing agent, added dropwise. The synthesis process and reaction mechanism are illustrated in Figure 1. Figure 1a-c shows the colour changes of the mixture during the reducing process. The colour of the final mixture is brown, due to the secondary colours of the products and the Mn coordination compound solution. The brown mixture was filtered, washed and dried; then, orange-yellow products were obtained, which can emit strong red light under blue or UV illumination. As reported in the literature, red-emitting Mn<sup>4+</sup>-activated fluoride phosphors are known to be yellow or light orange. The following characterisations also demonstrate that the orange-yellow products are K<sub>2</sub>TiF<sub>6</sub>:Mn<sup>4+</sup> phosphors. The most likely reaction mechanism (see Figure 1d) is the reduction of Mn<sup>7+</sup> to Mn<sup>6+</sup>, Mn<sup>5+</sup>, Mn<sup>3+</sup> or Mn<sup>2+</sup> by H<sub>2</sub>O<sub>2</sub>, but only Mn<sup>4+</sup> can replace Ti<sup>4+</sup> in the K<sub>2</sub>TiF<sub>6</sub> host because the Mn<sup>4+</sup> ion has an effective ion radius of r = 0.53 Å, which is easily substituted for the Ti<sup>4+</sup> ion (r = 0.61 Å) in the TiF<sub>6</sub><sup>4-</sup> octahedra, rather than the Mn<sup>3+</sup> ion (r = 0.83 Å), Mn<sup>5+</sup> ion (r = 0.65 Å) or Mn<sup>2+</sup> ion (coordination number = 4, r = 0.33 Å). The replacement of Ti<sup>4+</sup> in the K<sub>2</sub>TiF<sub>6</sub> host with the Mn<sup>4+</sup> in the solution is a cation exchange reaction, which facilitates the formation of Mn<sup>4+</sup> in the reduction reaction. In contrast to the traditional procedure, the above synthetic procedure is simplified, and the reduction reaction and cation exchange occur simultaneously to generate mutual promotion.

![Figure 1](image-url)
six-coordinated in the TiF$_6^{2-}$ octahedral structure, and the K$^+$ ion is surrounded by 12 nearest neighbour F$^-$, forming a three-dimensional framework. No traces of the Mn compound phase or other impurity peaks were observed. Nonetheless, the diffraction peaks of 2θ appear at 19.0°, 38.6° and 42.8°, assigned to the (0 0 1), (0 0 2) and (1 0 2) planes, whose intensities were distinctly weakened. To determine the cause of this result, we compared SEM images of the K$_2$TiF$_6$ powders and the synthesised K$_2$TiF$_6$:Mn$^{4+}$ (see Figure 4). The K$_2$TiF$_6$ particles and the synthesised K$_2$TiF$_6$:Mn$^{4+}$ particles have a similar size of 50-100 μm but different morphologies. K$_2$TiF$_6$ particles show an irregular disk-like morphology, whereas the synthesised K$_2$TiF$_6$:Mn$^{4+}$ particles display two morphologies of a sheet shape and an oblate sphere with a rough surface, resulting from the cation exchange and the HF corrosion. The decrease of the lattice planes in the reaction process leads to the morphological change of the synthesised K$_2$TiF$_6$:Mn$^{4+}$ particles. According to the literature, large micro-sized cube phosphors (~100 μm) are scatter-free, and their luminous efficacy and packaging efficiency are higher than those of commercial powdery phosphors.

To verify that the Mn$^{4+}$ ions were doped in the K$_2$TiF$_6$ host, unit cell refinements of the samples were performed using JADE software, which indicated that the fitted interplanar distance decreased from 2.173 Å for the raw K$_2$TiF$_6$ materials to 2.167 Å for the synthesised K$_2$TiF$_6$:Mn$^{4+}$(1.1 at.%). This result is consistent with the expected structural change induced by the substitution of the smaller Mn$^{4+}$ cation for the larger Ti$^{4+}$ cation in the crystalline lattice.

Figure 2. Images of the synthesised K$_2$TiF$_6$:Mn$^{4+}$ under room light (a) and UV light illumination (b). (c) Schematic of the crystal structure of a K$_2$TiF$_6$ unit cell. (d) XPS spectrum of the synthesised samples.

Figure 3. XRD patterns of samples synthesised by adding 0.064, 0.032, 0.021, 0.016, 0.013 g/ml (a-e) KMnO$_4$ and raw K$_2$TiF$_6$ materials (f).

Figure 4. SEM images of K$_2$TiF$_6$ powders (a, c) and the synthesised K$_2$TiF$_6$:Mn$^{4+}$(1.1 at.%) phosphors (b, d).

In the present work, the cation exchange procedure is a solid-liquid reaction, in which the diffusion of the Mn$^{4+}$ ion plays an important role. On the basis of Fick’s law, the diffusion flux is proportional to its concentration gradient, so the initial concentration of KMnO$_4$ in the HF solution should have a strong effect on the Mn$^{4+}$ doping percentage and the photoluminescence properties of the final products. The Mn$^{4+}$ doping percentage in K$_2$TiF$_6$ was estimated from the EDX results (see Figure 5). All energy peaks correspond to the elements in K$_2$TiF$_6$:Mn$^{4+}$, except for the
peaks at 0.25 and 0.5 keV, which correspond to organic matter from the preparation process. ICP–OES analyses reveal that the Mn⁴⁺ concentrations of the samples are 0.35–4.4 at.% (approximately 50 at.% Mn⁴⁺ reduced to Mn⁴⁺) and increase with an increasing initial KMnO₄ concentration. Monitored at 460 nm excitation, the synthesised K₂TiF₄:Mn⁴⁺ (1.1 at.%), shows a high internal quantum efficiency of 0.825 and an external quantum efficiency of 0.568, respectively.

**Figure 5.** EDX spectrum (a) of the synthesised K₂TiF₄:Mn⁴⁺ (1.1 at.%) and the dependence (b) of the Mn⁴⁺ concentration (at.% on the initial KMnO₄ concentration.

Mn⁴⁺ (3d⁹ configuration) in the crystalline host produces a strong crystal field due to its high effective positive charge. Therefore, the emission spectra of many Mn⁴⁺-activated red phosphors are dominated by the spin-forbidden ⁷E₆ 3→³A₂₂ transition (sharp line), such as Na₃SiF₆:Mn⁴⁺, Cs₂GeF₆:Mn⁴⁺, SrTiO₃:Mn⁴⁺, YAlO₃:Mn⁴⁺, and Y₃Sc₂O₅:Mn⁴⁺.²⁸,²⁹ The emission spectrum of the synthesised K₂TiF₄:Mn⁴⁺ consists of five narrow bands, extending from 580 to 660 nm, with the strongest peak at 634.8 nm (~2 eV) (see Figure 6b), assigned to the ⁷E₆ 3→³A₂₂ transition. Because the energy of the ⁷E₆ state in the d⁹ electronic configuration is independent of the crystal field (as demonstrated by Tanabe–Sugano diagrams), the increased width of the emission lines is not due to variations in the crystal field strength but can be explained by the strong electronic–vibrational interaction between the electronic states of the Mn⁴⁺ ions and crystal lattice vibrations. The two broad excitation bands peaking at ~365 nm (~3.5 eV) and ~460 nm (~2.7 eV) are attributed to the ³A₂₂→³T₂₂ and ³A₂₂→³T₂₂ spin-allowed transitions (see Figure 6a). The excitation and emission spectra of our synthesised K₂TiF₄:Mn⁴⁺ differ from those of CaAlN₃:Eu²⁺ red phosphors (see Figure 6a). The excitation bands of our synthesised K₂TiF₄:Mn⁴⁺, with peaks at ~460 nm, are more suitable for blue LED chips, and their emission bands fit well with the sensitivity curve of photopic human vision due to the lower emission beyond 650 nm, a range in which the human eye is insensitive.³⁰ The Mn⁴⁺ in K₂TiF₄:Mn⁴⁺ comes from the initial KMnO₄, which thus has an important influence on the relative emission intensity of the synthesised K₂TiF₄:Mn⁴⁺ phosphor (see Figure 7). The relative emission intensity of the sample first increases and then declines as the KMnO₄ concentration is increased, depending on the concentration quenching effect of the Mn⁴⁺ activator. The optimum KMnO₄ concentration is 0.016 g/ml. The intensity of K₂TiF₄:Mn⁴⁺ synthesised by a slow titration reaction is much greater than that obtained by a quick reaction due to the effect of the diffusion time.
To demonstrate the application of the synthesised K$_2$TiF$_6$:Mn$^{4+}$ red phosphors, white LEDs were fabricated with different weight ratios of the synthesised K$_2$TiF$_6$:Mn$^{4+}$ and blue chips (455 nm). Figure 9 shows CIE chromaticity coordinates (x, y) of the LEDs vary from the white light (0.344, 0.372) region for LEDs fabricated with only Y$_2$Al$_5$O$_{12}$:Ce$^{3+}$ phosphors. Table 1 compares relevant photoelectric parameters, such as the CCT, CRI and luminous efficacy, for the fabricated LEDs. The LED fabricated by combining a blue chip and a blend of K$_2$TiF$_6$:Mn$^{4+}$ red phosphor and Y$_2$Al$_5$O$_{12}$:Ce$^{3+}$ phosphor exhibited a lower CCT and a higher CRI than the LED with only the Y$_2$Al$_5$O$_{12}$:Ce$^{3+}$ phosphor due to the additional red light component in the emission spectrum of the LED, which can be confirmed by the electroluminescence spectra (see Figure 9b). After adding the synthesised K$_2$TiF$_6$:Mn$^{4+}$, the white LED has a high CRI (Ra $>$ 85), which is suitable for indoor lighting. Moreover, the luminous efficacy of the white LED with the synthesised K$_2$TiF$_6$:Mn$^{4+}$ remains almost the same, although the yellow component of its spectrum weakens due to the decreased amount of Y$_2$Al$_5$O$_{12}$:Ce$^{3+}$ phosphor.

4. Conclusions

On the basis of the reduction reaction of KMnO$_4$ (Mn$^{7+}$) to Mn$^{2+}$, we synthesised K$_2$TiF$_6$:Mn$^{4+}$ phosphors by a simple chemical reaction using K$_2$TiF$_6$ particles immersed in KMnO$_4$/HF solution. The obtained K$_2$TiF$_6$:Mn$^{4+}$ phosphors have a size of 50-100 μm. The Mn$^{4+}$ concentrations in the K$_2$TiF$_6$ host are 0.35- 4.4 at.% (approximately 50 at.% Mn$^{7+}$ reduced to Mn$^{4+}$). The Mn$^{4+}$ concentration in K$_2$TiF$_6$ increases with increasing initial KMnO$_4$ concentration, subject to diffusion of the Mn$^{4+}$ ion. However, the relative emission intensity of the sample first increases and then declines as the KMnO$_4$ concentration is increased, with an optimum KMnO$_4$ concentration of 0.016 g/ml, depending on the concentration quenching effect. The synthesised K$_2$TiF$_6$:Mn$^{4+}$ phosphor has excellent thermal stability and was used to produce high-CRI (Ra $>$ 85) white LEDs that are suitable for indoor lighting.

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Notes and references


Large micro-sized $K_2TiF_6: Mn^{4+}$ red phosphors synthesised by a simple reduction reaction for high colour-rendering white light-emitting diodes.